

# **ALKALINE PULPING: DEADLOAD REDUCTION STUDIES IN CHEMICAL RECOVERY SYSTEM**

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# **ALKALINE PULPING: DEADLOAD REDUCTION STUDIES IN CHEMICAL RECOVERY SYSTEM**

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## SUMMARY

The kraft pulping process has been known for decades. The focus in kraft pulping has always been on better operation of the chemical recovery system. One of the targets is on deadload (sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ )) reduction in white liquor. A model based on several literature references was developed to study the effect of deadload reduction. A base model was developed based on current mill operation. This base model was compared to the deadload reduction model. Overall improvement, such as operating cost saving and revenue generation was achieved from deadload reduction. Operating cost saving involves less deadload chemical in chemical recovery system, and less water that was associated with the deadload itself. Revenue generation involves generating more steam and heat from the recovery boiler that can be used for mill purposes or energy revenue. Two important variables to achieve deadload reduction are causticizing efficiency and reduction efficiency.



## **CHAPTER 1**

### **INTRODUCTION**

Kraft pulping is a well known pulping process. The first chemical pulping process using soda was patented in 1854. This process was first commercially used in Sweden in 1884. Since this process was invented, the economical recovery of pulping chemicals became a primary focus. To be able to compete with the other processes such as the sulfite process which doesn't have a recovery system, the kraft process enables most of the pulping chemicals to be recovered and reused to reduce production cost.

Several inventions, such as the recovery furnace and chlorine dioxide bleaching, mark the major advancement for kraft pulping process. In 1930, the recovery furnace was introduced. This is where final evaporation and burning of used or spent liquor, heat recovery, and chemical recovery were combined in one unit. And in 1950, chlorine dioxide bleaching was developed, improving the kraft brightness level.

The kraft chemical recovery process primarily converts black liquor (spent liquor) into white liquor that can be reused for pulp cooking. The black liquor is converted into sodium carbonate and sodium sulfide in the recovery boiler. Sodium carbonate in the green liquor from the smelt dissolving tank is reacted with quicklime to form sodium hydroxide (major component in white liquor) and calcium carbonate (lime mud). The white liquor is separated from the mud and sent to the digester as cooking liquor. The mud is washed to recover soda values and calcined to form quicklime ( $\text{CaO}$ ), which is recycled.

## 1.1 Terms and Definitions

To understand the concept of the pulping process, TAPPI terms and definitions will be used. Several terms such as white, black, and green liquor are common being used in the combustion, reduction, causticizing, and calcining cycle. The following will discuss several terms that will be used:

- White liquor is fresh pulping liquor that is used for the Kraft process. White liquor consists of the active pulping chemicals, such as NaOH, Na<sub>2</sub>S, and small amounts of Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> left over from recovery process.
- Black liquor is waste liquor from the pulping process after pulping is completed. This black liquor contains: organics (dissolved wood component) and inorganic components (cooking chemicals). For each ton of pulp produced, 3000-5000 gallons or about 7 tons of black liquor are produced at 15% solids [8]. This black liquor must be concentrated to as high a solids content as possible before being burned in recovery boiler. Black liquor is usually burned at 65-75% solid content.
- Green liquor is produced by dissolving smelt from the recovery boiler (Na<sub>2</sub>S, Na<sub>2</sub>CO<sub>3</sub>, and inerts) in water. After further processing, green liquor is converted to white liquor which can be used again for pulping.
- Total chemical, or total alkali (TA), is the sum of all sodium salts in liquors (as Na<sub>2</sub>O) that contribute to AA (i.e. NaOH + Na<sub>2</sub>S) or are capable of being converted to AA in the kraft cycle.

$$TA = NaOH + Na_2S + Na_2CO_3 + Na_2S_xO_y \text{ (as } Na_2O \text{)}$$

Table 1: Composition of Liquors in Kraft Cycle [9]

No.	Content	White liquor	Black liquor	Green liquor
		% total	% total	% total
1	NaOH	53	6	8
2	Na <sub>2</sub> S	21	19	52
3	Na <sub>2</sub> CO <sub>3</sub>	15	36	60
4	Na <sub>2</sub> SO <sub>3</sub>	3	9	3
5	Na <sub>2</sub> SO <sub>4</sub>	5	13	6
6	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	3	16	3

- TTA is the sum of all of the bases in the white liquor that can be titrated with strong acid.

$$TTA = NaOH + Na_2S + Na_2CO_3 \text{ (as } Na_2O \text{)}$$

- Active alkali or AA is the active ingredients in the pulping process

$$AA = NaOH + Na_2S$$

- Effective alkali, or EA, is the ingredients that will actually produce alkali under pulping conditions.

$$EA = NaOH + \frac{1}{2} Na_2S$$

- Sulfidity is the ratio of Na<sub>2</sub>S to the active alkali, usually expressed as percent.

$$\text{Sulfidity} = \frac{Na_2S}{NaOH + Na_2S} \text{ (as } Na_2O \text{)}$$

- Causticity is the ratio of NaOH to active alkali.

$$\text{Causticity} = \frac{NaOH}{NaOH + Na_2S} \quad (\text{as } Na_2O)$$

- Causticizing efficiency is the ratio of NaOH to NaOH and Na<sub>2</sub>CO<sub>3</sub> (as Na<sub>2</sub>O).

This is used as a measurement of how efficient the causticizing process is.

$$\text{Causticity efficiency} = \frac{NaOH - NaOH_{in \text{ green liquor}}}{NaOH + Na_2CO_3 - NaOH_{in \text{ green liquor}}} \times 100\% \quad (Na_2O \text{ basis})$$

- Reduction efficiency is the ratio of Na<sub>2</sub>S to Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>4</sub> in green liquor.

This is a measurement of reduction efficiency of sulfur species in the recovery boiler.

$$\text{Reduction efficiency} = \frac{Na_2S}{Na_2S + Na_2SO_4} \times 100\% \quad (\text{mole basis})$$

## 1.2. Deadload

In the kraft pulping process, liquor chemicals other than the active cooking chemicals are considered to be deadload [14]. The active cooking chemicals in kraft pulping are sodium hydroxide (NaOH) and sodium sulfide (Na<sub>2</sub>S). While reusing the pulping chemicals from the recovery process, several inactive chemicals or deadloads (sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>)) are formed.

## 1.3. Model and Study

To study the deadload effect in the liquor cycle, a steady state model was developed. The simulation of the model is based on material balances and designed to predict the effects of reducing Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> on different unit processes in a kraft pulp mill.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1. Pulping**

Pulping is the process by which wood is reduced to fibrous mass. It is the means of breaking bonds within the structure of wood to separate fibers. There are two types of pulping, chemical and mechanical pulping. Several combinations of these two are also found in the process such as chemimechanical and semi-chemical pulping.

Mechanical pulping is the type of pulping that uses mechanical energy with the use of little or no chemical in process. This mechanical pulp is made by 2 processes:

- Grinding: logs of wood are ground with revolving abrasive stone (SGW)
- Refining: wood chips are fed between two metal discs, with one of them rotating (RMP)

On the other hand, chemical pulping is type of pulping that uses chemicals and heat to dissolve lignin. Usually this process leaves only cellulose and hemicelluloses. Three major types of chemical pulping are kraft, soda, and sulfite pulping.

Table 2 shows the different types of pulping:

Table 2: Comparison of Different Pulping Processes [17]

Mechanical	Hybrid	Chemical
Pulping by mechanical energy (little or no chemicals and heat)	Pulping with combinations of chemical and mechanical pulping	Pulping with chemical and heat (little or no mechanical mean)
High yield (90-95%)	Intermediate yield (55-90%)	Low yield (40-50%)
Short, impure fibers - weak - unstable	Intermediate pulp properties	Long, pure fibers - strong - stable
Good print quality		Poor print quality
Difficult bleaching		Easy bleaching

## 2.2. Kraft Pulping

The word ‘kraft’ means ‘strong’ in German. This type of pulping is usually found in North America. Although the yield is low, recovery technology in kraft pulping is proven. Several products from kraft pulp include linerboard, xerographic, and food boards.

In kraft pulping, two chemicals that are used are sodium hydroxide (NaOH) and sodium sulfide (Na<sub>2</sub>S). The operation of kraft pulping is as follows [2, 17]:

- Chemicals and chips are charged into the digester, continuous or batch
- Usually, temperature is raised to 170 C
- Cooked for 2 to 4 hours depending on lignin removal desired

- Pulp and black liquor are blown at the end of the cook
- Black liquor consists of used chemicals, carbohydrates, and dissolved lignin

### 2.3. Chemical Recovery

Chemical recovery in kraft pulping has been the focus through the decade because of the large volume that is being produced. As mentioned before, each ton of pulp produced, 3000-5000 gallons or about 7 tons of black liquor produced at 15% solids.

The kraft recovery system has three main functions [9]. They are:

- Recovery and reuse of the inorganic pulping chemicals
- Removal and sale of valuable organic by-product chemicals
- Destruction of remaining organic material and recovery of its energy value as process steam and electrical power

Figure 1 shows the chemical recovery cycle diagram.

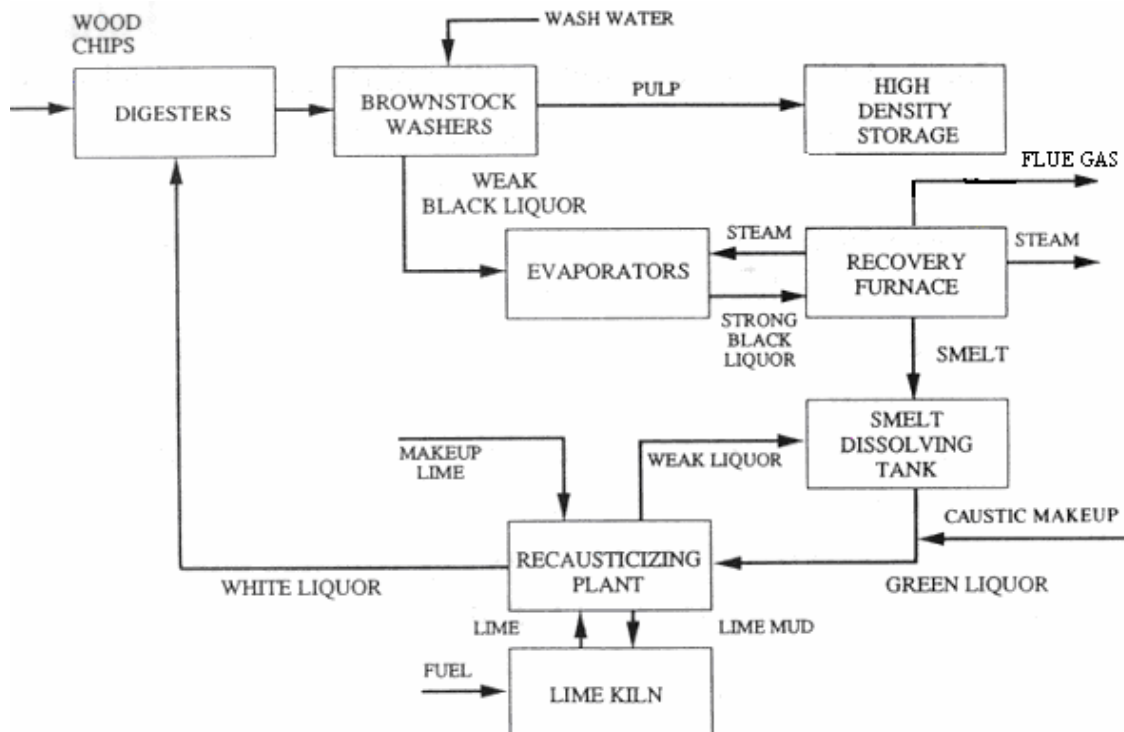


Figure 1: Block Flow Diagram of Kraft Chemical Recovery [8]

## 2.4. Deadload

According to Blackwell and MacCallum, about fifty-percent of North America's kraft mills are restricted in production by the rate of formation of fireside deposits in the recovery boiler. One of the causes of this is the deadload of inactive and inert inorganic chemicals in kraft liquor cycle. The most common of deadload chemicals are sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and sodium sulfate ( $\text{Na}_2\text{SO}_4$ ). Sodium sulfate in white liquor comes from incomplete reduction in the furnace or recovery boiler and oxidation of  $\text{Na}_2\text{S}$  in recausticizing. Carbonate in white liquor comes from incomplete conversion in the causticizers [4, 7]. Sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) generally accounts for most of the deadload, while sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) is about one-fourth of carbonate amount [14].

Other deadload in kraft liquor includes unreacted calcium oxide ( $\text{CaO}$ ),  $\text{Ca}(\text{OH})_2$ , inert compounds containing Na, Mg, Fe, Mn, aluminum complexes, silica complexes, chloride, phosphate, and sulfate [3]. These deadload species enter the process with the wood, process water, and make-up limestone. However, the amount of these other compounds is generally much smaller than sodium carbonate and sodium sulfate.

According to Keitanniemi and Virkola, about 20 to 25% of inorganic chemicals circulating in the liquor cycle are present as deadload. About two-thirds of it is sodium carbonate and the rest is sodium sulfate [20].

## 2.5. Deadload impact on process equipments

Deadload inorganic chemicals can affect the chemical recovery system costs in several ways. Several major aspects that were known are [3,7]:

- Restriction in capacity of process equipment, especially recovery boilers.
- Increased recovery boiler total reduced sulfur (TRS) emissions.



- Energy consumed to heat, evaporate and pump the associated water.
- Added evaporation requirement in kiln.
- Increased make up requirements because of higher chemical losses.
- Higher cleaning costs resulting from scale in evaporators.

For details, the following sections will analyze the effect or impact of deadload on process equipment.

### **2.5.1. Digester**

Wood and white liquor ( $\text{NaOH}$  and  $\text{Na}_2\text{S}$ ) are reacted in the digester at about 170 C to produce kraft pulp and weak black liquor. Several by-products such as turpentine and non-condensable gases will be recovered from the digester also.

While there is no effect of deadload on the pulp production process, several aspects that are impacted by the deadload in the digester operation are [7]:

1. The heat load for taking the inerts and their associated water up to the cooking temperature.
2. Reduced capacity in digester because of the physical space that was taken by the inerts and their water.
3. White liquor concentration or black liquor concentration recirculation limitation to keep the dissolved solids concentration in the black liquor in the chips below the point where soap precipitates. Soap precipitation is determined by the concentration of sodium counterion; thus, this will increase with inorganic deadload.

### **2.5.2. Washer**

Weak black liquor is separated from pulp at the washers. The black liquor is diluted by the wash water. Modern pulp washing normally recovers at least 98% of the chemicals applied in digester [9].

Several aspects causing inefficiency in the washer because of deadload are:

1. Increased washing losses (the amount of inorganic chemical leaving the pulping and recovery system with the washed pulp).
2. More wash water is required to achieve a better washing efficiency. Thus, this will increase the evaporation loads and energy consumption in evaporators.

### **2.5.3. Evaporators and Concentrators**

The evaporation or concentration of black liquor is carried out in multiple effect evaporators using low pressure steam. A modern evaporator normally consists of six effects with an economy of about 4.8 lb of water evaporated per lb of steam. Concentrators consist of two or three units with an economy of about 1.8 lb of water evaporated per lb of steam. These units generate concentrated black liquor that will be charged into the recovery boiler.

Deadload has a direct effect on evaporation operations such as [3,7]:

1. Increased steam consumption to evaporate water that carries deadload and additional wash water from washing operation.
2. Increased boiling point rise of the liquor. This boiling point rise is proportional to inorganic concentration, thus will go up directly with deadload.

3. Increased scaling problems. A double salt,  $2\text{NaSO}_4 \cdot \text{Na}_2\text{CO}_3$ , can precipitate from black liquor at solids concentration of 50%. This will result in reduction of productivity.

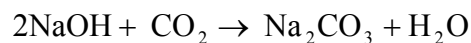
#### 2.5.4. Recovery Boiler

The development of the recovery boiler in 1930 led to the predominance of the kraft process. The purpose of the recovery boiler is to recover the inorganic chemicals as smelt (sodium carbonate and sodium sulfide), burn the organic chemicals so they are not discharged from the mill as pollutants, and recover the heat of combustion in the form of steam.

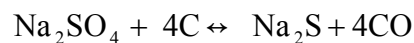
This recovery boiler is the largest and most expensive piece of equipment in the kraft mill. The cost of this equipment is over \$100 million [8]. Nowadays, recovery boilers can support 2500-3000 tons of pulp production per day [8, 10].

In addition to combustion reactions, the overall chemical reactions in the recovery boiler are:

1. Conversion of sodium salts:

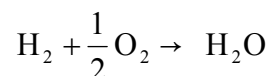
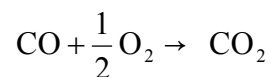


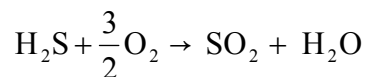
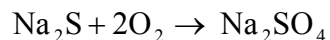
2. Reduction of make-up chemical:



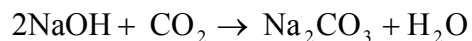
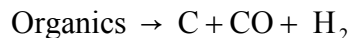
For more details of the reaction, there are 3 known zones of reaction

- a. Oxidation zone:

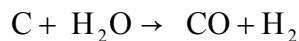
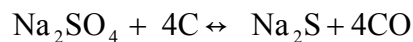
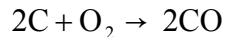
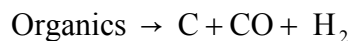




b. Drying zone:



c. Reduction zone:



The impacts of deadload on the recovery boiler are as following [2, 3, and 7]:

1. With deadload presence, the ratio of organics to inorganics in the liquor decreases. Thus, it decreases the higher heating value per kg of total solids.
2. The increased ash content of the liquor with deadload presence means that more inorganic material leaves the recovery boiler entrained in the exit gas.
3. Increased TRS emission.
4. Lower reduction efficiency

#### **2.5.5. Dissolving Tank or Smelt Tank**

Weak Wash from mud washer fills the dissolving tank, which is usually located below the Kraft recovery furnace, where the molten smelt is added from the smelt spout to form green liquor (mainly  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{S}$ ).

The presence of deadload in smelt will result in increasing the melting point and viscosity of smelt. This will make smelt handling harder [4].

#### **2.5.6. Green Liquor Clarifier**

The green liquor clarifier is a settling tank used to remove dregs by sedimentation before the green liquor is recausticized. This clarifier can also serve as a storage tank for green liquor and can provide at least 12 hours supply of green liquor [2, 9]. The dregs settle to the bottom where rakes move them to outlets. If there is no or inadequate green liquor clarification, the inert materials build up in the lime, hence decreasing the lime availability.

While the presence of deadload in the green liquor clarifier is minimal, one of the most significant impacts is decreasing capacity of the clarifier. More deadload will result in requiring a bigger volume for sedimentation at constant TTA [2, 7].

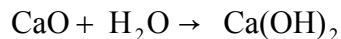
#### **2.5.7. Dregs Filter or Washer**

Dregs are undissolved materials in the green liquor. The dregs are about 0.1% of the liquor and consist of carbon (20% or more) and foreign materials (mainly insoluble metal carbonates, sulfates, sulfides, hydroxides, and silicates) to give a black bulky material [2]. Many believe that the source of dregs is from incomplete combustion of organic materials in recovery furnace. These dregs are washed in a dregs washer, often a drum filter or sedimentation washer.

Several references [2, 3, and 7] explain that reduction of deadload will reduce amount of dregs which must be transferred to landfill.

### 2.5.8. Slaker

The slaker is a chemical reactor in which lime is mixed with green liquor. The reaction temperature is 99-105 C [2]. Using a high temperature lime directly from kiln gives a lime mud that settles well. The lime, CaO, forms slaked lime, Ca(OH)<sub>2</sub>, and much of the causticizing reaction occurs here. This slaking reaction is as following

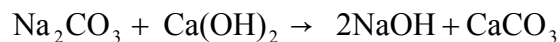


Grit is removed here by the classifier section. Grits are unreactive lime particles and insoluble impurities. Grit accounts for 0.5 to 2% of the lime feed and are often sent to landfills.

One main impact of deadload presence in the slaker is to limit the slaker capacity because it and its associated water occupy space in the slaker [3, 21].

### 2.5.9. Causticizers

Causticizers are two to four continuous flow, stirred reactors that are used to complete the causticizing reaction. The following shows the causticizing reaction



The extent of the causticizing reaction depends on the concentration of the initial Na<sub>2</sub>CO<sub>3</sub> and the amount of lime used. With the concentration of actual chemical below 16%, the theoretical conversion is over 90% [17]. At concentrations above this, the theoretical conversion drops quickly. For this process, usually it desired to have about 1% excess lime. The causticizing efficiency should be 3-4% below the equilibrium value if excess liming is avoided.

The impacts of deadload on causticizers are as follows [2, 3, and 7]:

1. Lower causticizing efficiency

2. Probable increased in a scaling problems
3. Loss in causticizing capacity because of the inert deadload and its associated water which occupies space in causticizers.

#### **2.5.10. White Liquor Clarifier**

The white liquor clarifiers are settling tanks (gravity sedimentation) used to remove the lime mud ( $\text{CaCO}_3$ ) from the white liquor. The lime mud usually leaves with a solid content above 35% in order to minimize entrained soda that is removed in the lime mud washer.

Poor settling lime may be the result of excess lime to the slaker (more than 1% excess), a low lime availability (below 80-85% is indicative of a high level of contaminants due to inadequate removal of dregs and/or grit or incomplete slaking due to overloading the lime kiln), a high percentage of low reactivity unburned fresh lime, or inadequate white liquor clarification [2, 9]. Lime burned at too low a temperature gives mud of high viscosity; lime burned at too high a temperature gives a slow causticizing reaction and a slow settling lime mud with entrained alkali.

One of the known impacts of deadload presence in the clarifier is limited capacity because of it and its associated water occupies space in clarifier [3, 21].

#### **2.5.11. Lime Mud Washer**

The lime mud washer removes most of the 15-20% of entrained alkali ( $\text{Na}_2\text{O}$  basis) from the lime mud, usually by sedimentation washing [2]. This lime mud wash is typically a settling tank (or two in series) where fresh (make-up) water is used to wash the lime mud. If it were not removed, the  $\text{Na}_2\text{S}$  would cause slagging in the kiln and reduced sulfur compounds would be released as  $\text{H}_2\text{S}$ . Usually about 1% of alkali on lime

mud remains after washing. The liquor (known as weak wash) is used to dissolve smelt from recovery boiler. A proper balance of water is important during lime mud washing to avoid formation of excess weak wash.

The impacts of deadload on mud washers are as following [2, 3, and 7]:

- More thorough washing is needed to reach the same residual sodium level in the mud.
- Minor effect on capacity limitation

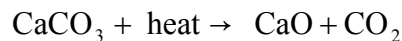
#### **2.5.12. Lime Mud Filter**

Thick lime mud from storage is diluted to 25-30% solids before going to the lime mud filter [9]. The lime mud filter is a rotary drum vacuum filter washer used for final lime washing and thickening to 60-70% solids before the lime enters the kiln.

Not much detail has been reported about the impact of deadload on mud filter performance.

#### **2.5.13. Lime Kiln**

The lime kiln is a chemical reactor in which lime mud ( $\text{CaCO}_3$ ) is dried, heated, and converted to  $\text{CaO}$ . This process is also known as calcining.



Fuel oil or natural gas (or occasionally coal or biomass) supplies the fuel to achieve the high temperature (1200 C) required [2, 17]. The combustion gases run counter-current to the lime flow.

The purity of the lime is given by lime availability and is defined as

$$\text{Lime availability} = \frac{\text{CaO}}{\text{lime}} \text{ (as mass ratio)}$$



The main disadvantage of deadload in the kiln is that it carries water into the kiln; this will add to evaporation requirements [16], resulting in an increase of fuel consumption and a decrease of kiln capacity.

## **2.6. Process control**

With many types of equipment that are used in this chemical recovery system, complex process control using a computerized system has been implemented to control deadload in the system. In general, the following overall objectives are optimized by the control system [9]:

- Steady and satisfactory white liquor quality
- Adequate production capacity
- Minimum energy consumption
- Minimize deadload chemicals in white liquor
- Meet air emissions requirements
- Minimum downtime
- Minimize chemical losses

## CHAPTER 3

### MODEL AND ASSUMPTION

The purpose of this study is to evaluate and analyze the result of deadload reduction in the white liquor supplied to the digester. To achieve this result, a base model was developed to analyze the effect of deadload reduction.

#### 3.1 Model

A detailed computer simulation model of the kraft liquor cycle has been constructed in a Microsoft Excel<sup>®</sup> spreadsheet for simplification and easy editing. This model was developed based on operating experience [1, 8, 9, and 19]. The simulation encompasses evaporators, concentrators, recovery boiler, recausticizing, and lime kiln.

For details, figure 2 shows the process block diagram that was used in this model. To understand the heat balance in the recovery boiler, a heat balance calculation was added in this model as well. A Black liquor higher heating value of 6300 btu/bls for the base model was assumed.

This simulation depends on two important parameters which determine the amount of deadload, namely causticizing efficiency and reduction efficiency. These parameters were defined in chapter 2.

The slaking/ causticizing process is modeled according to slaking and causticizing reactions (chapter 2). These reactions proceed simultaneously in the slaker and causticizers. Some slaked, uncausticized lime ( $\text{Ca(OH)}_2$ ) passes through the causticizers and is eventually recycled to the lime kiln.

The reduction reaction in the recovery boiler is as follows:

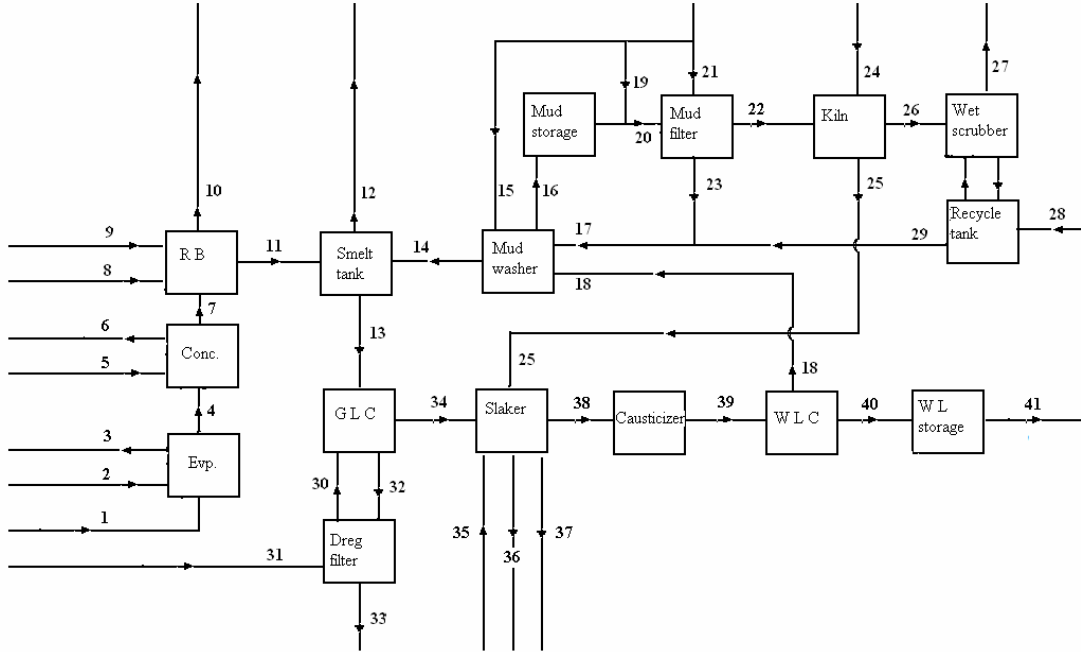
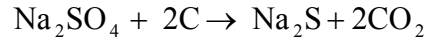


Figure 2: Chemical Recovery Cycle

### 3.2. Base Assumption

Table 3 shows base assumption for this liquor recovery cycle model. Details of the assumptions are shown in the appendix.

From Table 3, the specific gravity for this model was assumed constant. This might not be a real assumption, with the reduction of deadload; one can expect specific gravity will decrease. However, for simplification of this study, specific gravity will be assumed constant.

Table 3: Base Assumption

<b>Base Parameter</b>	<b>Amount</b>	<b>Unit</b>
1 o.d. ton dry unbleached pulp	2000.0	lb
Pulp yield	48.0	%
AA on o.d. wood	16.5	%
White Liquor activity	85.0	%
Sulfidity	25.0	%
White Liquor total alkali	7.5	lb/ft <sup>3</sup>
Excess lime	2.0	%
Lime Availability	85.0	%
Specific gravity of white liquor	1.13	
Na <sub>2</sub> SO <sub>4</sub> /Na <sub>2</sub> S ratio	0.2	
Density of Water	62.4	lb/ft <sup>3</sup>
Specific gravity of green liquor	1.16	
Mud solid underflow	40	%
Fuel requirement in Lime kiln	0.18	lb/ lb CaO
Fuel/ air ratio in kiln	0.06	lb/ lb air
Grit solid in purge	60	%
% Solid from concentrator	70	%
Concentrator steam economy	1.8	
Evaporator steam economy	4.8	

### 3.3. Deadload reduction study

With the base case values set as in table 3, a new case, or deadload reduction case, was developed for comparison. This new case has a different composition of white liquor chemical, notably the amount of deadload in the liquor. Active alkali composition will remain the same. Details of chemical recovery system are summarized in chapter 4. Table 4 shows this comparison.

Table 4: Comparison between Base and New

Chemicals	Base (lb as Na <sub>2</sub> O)	New (lb as Na <sub>2</sub> O)
Na <sub>2</sub> S	171.88	171.88
NaOH	515.63	515.63
Na <sub>2</sub> CO <sub>3</sub>	121.32	<b>57.00</b>
Na <sub>2</sub> SO <sub>4</sub>	18.88	<b>9.44</b>

From Table 4, the amount of Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> was reduced approximately 50% each. From these new values, several observations regarding the process improvement will be presented.

## CHAPTER 4

### RESULTS AND DISCUSSIONS

Using the definitions of the base model case and the new model case, comparison between both cases was done. Several aspects such as white liquor requirement, green liquor composition, and black liquor composition were analyzed to understand more about the effect of deadload reduction.

#### 4.1. White liquor

One of the most important aspects of the chemical recovery system is the white liquor composition that was charged to the digester. Tables 5 and 6 show the comparison of these two conditions. The amount of water that is carried to the digester will be reduced by 7.3 % (6472 to 6000 lb) and the white liquor solids will be reduced by 11.6% (1132 to 1000 lb).

Table 5: White Liquor Comparison

Chemicals	Base	New	unit
Na <sub>2</sub> S	216.23	216.23	lb
NaOH	665.32	665.32	lb
Na <sub>2</sub> CO <sub>3</sub>	207.42	97.45	lb
Na <sub>2</sub> SO <sub>4</sub>	43.25	21.62	lb
Water	6472.01	5998.87	lb

Another important aspect of this reduction is a higher white liquor activity, which is the ratio of active alkali to total alkali. This is due to the fact of deadload reduction lowering TTA. The causticizing efficiency of the chemical recovery system is also

improved to 87.90% from 77.67%. The white liquor volume charged to digester decreases, thereby opening up the possibility for increased capacity. Details about the white liquor are shown in Tables 5 and 6.

Table 6: Comparison of White Liquor Operation Condition

Description	Base	New	unit
White Liquor activity	85.00	92.34	%
Na <sub>2</sub> SO <sub>4</sub> /Na <sub>2</sub> S ratio	0.20	0.10	-
AA as Na <sub>2</sub> O	687.50	687.50	lb
White Liquor TTA	808.82	744.50	lb
White Liquor Volume	107.84	99.27	ft <sup>3</sup>
Causticizing efficiency	77.67	87.90	%

#### 4.2. Green Liquor

In the chemical recovery system, usually the green liquor TTA is controlled. A similar result to the white liquor composition was achieved for the green liquor composition. With the reduction of white liquor deadload, the deadload in the green liquor was reduced as well. The amount of water in green liquor itself is reduced by 6.0% (from 7833 to 7368 lb) and the green liquor solids will be reduced by 9.0% (1561 to 1421 lb).

The reduction efficiency has to have been increased (presumably accomplished by recovery boiler operating changes) because of the deadload reduction that was assumed in the white liquor. As this reduction efficiency is a measure of amount of sodium sulfide to the total sodium sulfate and sodium sulfide, the reduction of sodium sulfate will

increase reduction efficiency. Also, the volume of green liquor will decrease by 6.7%.

Details about the green liquor are shown in Tables 7 and 8.

Table 7: Green Liquor Comparison

Chemicals	Base	New	unit
Dregs	7.22	7.22	lb
Na <sub>2</sub> S	255.45	258.83	lb
NaOH	120.66	131.09	lb
Na <sub>2</sub> CO <sub>3</sub>	1126.60	998.20	lb
Na <sub>2</sub> SO <sub>4</sub>	51.09	25.88	lb
Water	7833.24	7368.28	lb

Table 8: Comparison of Green Liquor Operation Condition

Description	Base	New	unit
% SO <sub>4</sub> <sup>2-</sup> reduction	90.10	94.79	%
GL TTA	955.51	891.19	lb
Volume GL	127.40	118.83	ft <sup>3</sup>

### 4.3. Black Liquor

A similar result was achieved with the black liquor composition after deadload reduction. The amount of black liquor solids will decrease from 2673 to 2546 lb. This 4.8% reduction occurs due to reduction of deadload chemicals in the white liquor that was charged to digester. The amount of water in the black liquor is decreased as well by 4.8% from 13051 to 12431 lb.



Table 9: Black Liquor Comparison

Chemicals	Base	New	unit
Na	588.08	534.33	lb
C	984.77	936.69	lb
H	93.56	93.73	lb
S	80.23	75.49	lb
O	919.28	898.73	lb
inert	7.22	7.23	lb
Water	13051.20	12431.50	lb

Table 10: Black Liquor Elemental Analysis Comparison

Chemical	Base	New	unit
Na	22.00	20.99	%
C	36.84	36.79	%
H	3.50	3.68	%
S	3.00	2.96	%
O	34.39	35.30	%
Inert	0.27	0.28	%

Table 11: Recovery Boiler Operation Condition

Description	Base	New	unit
Black liquor Heating Value	6300	6614	Btu/lb
Heat to steam generation	1.229E7	1.243E7	Btu

One of the most important features in this deadload reduction is the increase in higher heating value due to lower black liquor inorganics. Table 11 shows how this deadload reduction affects the recovery boiler operation. Heat-to-steam generation from the recovery boiler is increased as well by 1.1% from 1.229E7 to 1.243E7 Btu. This is important, since it will generate more revenue and reduce some operational cost.

#### **4.4. Evaporator and concentrator**

With less black liquor solids (BLS) that are produced, the water that carries the black liquor solids is less as well. This can be seen in the evaporator and concentrator profile in the following tables. This means that the steam that is used to evaporate the water will be less.

Table 12: Concentrator Profile

Description	Base	New	unit
Steam	1485.08	1414.56	lb
Energy usage	1.78E+06	1.69E+06	BTU

Table 13: Evaporator Profile

Description	Base	New	unit
Steam	2719.00	2589.90	lb
Energy usage	3.19E+06	3.04E+06	BTU

#### 4.5. Mud cycle - kiln

The mud cycle operation which was also analyzed in this study didn't show any changes with deadload reduction. Several studies have shown that there is either little or no effect on the lime mud cycle in the chemical recovery system [14, 16].

Table 14 and 15 show the inlet and outlet material balance comparison.

Table 14: Inlet Material Balance in Kiln

Description	Base	New	unit
CaCO <sub>3</sub>	928.36	928.36	lb
inert	82.99	82.99	lb
water	337.12	337.12	lb
fuel	79.24	79.24	lb
air	1260.38	1260.38	lb

Table 15: Outlet Material Balance in Kiln

Description	Base	New	unit
CaO	448.93	448.93	lb
inert	83.83	83.83	lb
dust	125.86	125.86	lb
CO <sub>2</sub>	352.73	352.73	lb
combustion product	1339.61	1339.61	lb
water	337.12	337.12	lb

#### 4.6. Energy

With less inorganic BLS that are produced with reduced deadload, more recoverable energy from the recovery boiler can be expected. Also, less energy will be used by the concentrator and evaporators because of less black liquor solids and the water associated with them. The total effect is a 5.2% increase in net energy generation. Table 16 shows the energy comparison for these two cases.

Table 16: Energy Generation Comparison

Description	Base	New	unit
Total Energy Going Outside Recovery Process	7.32E+06	7.70E+06	BTU

#### 4.7. Constant Density

Basic assumption that was stated in chapter 3 about constant density or specific gravity is likely shortcoming in this model. This assumption doesn't fit the real world operation. The water that associated with inorganic solids is directly calculated from this density assumption. This density also shows interdependency with total alkali. Lack of information (between density and total alkali) and calculation of water forced of this density assumption.

However, one can argue the deadload reduction is small (about 64 lb of  $\text{Na}_2\text{CO}_3$  and 9.4 lb of  $\text{Na}_2\text{SO}_4$ ); hence there is no effect on the model itself. Therefore, constant density that was used in the algorithm in Microsoft excel is valid.

## CHAPTER 5

### CONCLUSION

A first principles model was developed to study the effect of white liquor deadload reduction on process performance. The process equipment impacted include evaporators, concentrator, recovery boiler, smelt tank, lime mud clarifier, lime mud washer, lime mud filter, kiln, dregs washer, green liquor clarifier, slaker, causticizer, and white liquor clarifier. This model was developed based on a set of assumptions that was based upon literature references [1, 8, 9, and 19] and fundamental engineering principles.

Deadload in white liquor, green liquor and black liquor is reduced. Thus, water that carries the deadload is also decreased. This will improve the energy performance and loading performance of the equipment. Several operating costs, such as steam requirement for concentrator and evaporators, can be cut, since less chemical is cycled around the chemical recovery system. From the recovery boiler stand point, more energy can be produced with less deadload in system.

The two most important variables to determine the effect of deadload reduction are

- Causticizing efficiency  $\rightarrow$  sets the amount of  $\text{Na}_2\text{CO}_3$  in the liquor
- Reduction efficiency  $\rightarrow$  sets the amount of  $\text{Na}_2\text{SO}_4$  in the liquor

## **CHAPTER 6**

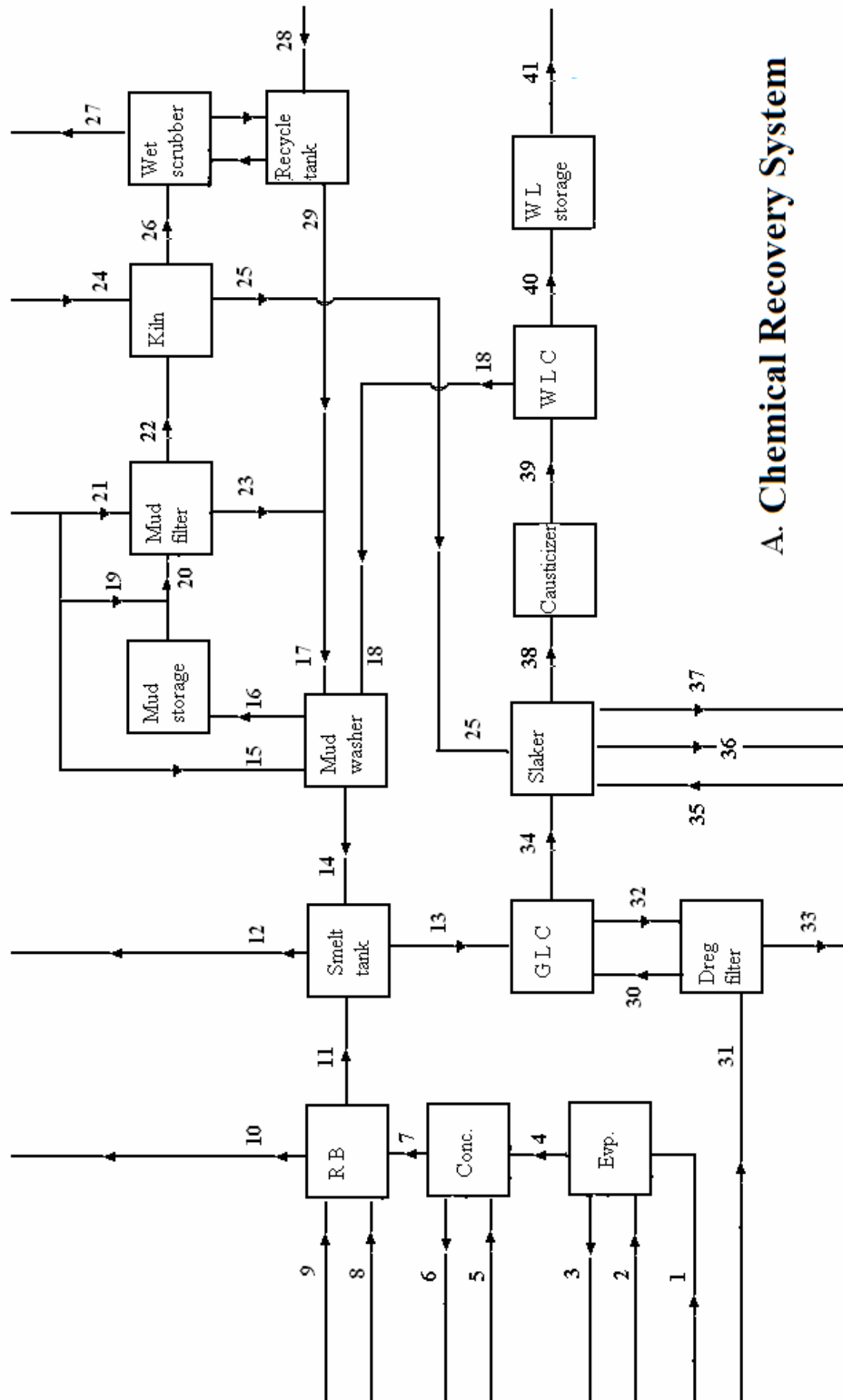
### **FUTURE WORKS**

The reduction of deadload in kraft pulping and chemical recovery can be very beneficial. Many pulp mills in North America need to reduce the operation cost of the mill to be able to compete with newer mills. These results can point to ways to achieve better operation in the chemical recovery system. While operating costs of process equipment can be cut drastically, other effects such as a potential capacity increase and process improvements can be achieved.

Several assumptions were used in this model that are based on fundamental engineering principles. Because the assumption of constant density or specific gravity doesn't fit the real world operation, a detailed study of liquor density would be beneficial to give a more rigorous model. An expanded model featuring an overall heat balance will also give a better insight to the chemical recovery system, yielding a more accurate model to predict the energy benefits of deadload reduction.

Another important outgrowth of this work would be to test the model results against mill data.

### A. Chemical Recovery System



## B. ALGORITHM

### 1. Entry & Assumption

	A	B	C	D
1		<b>Enter the Amount of Na<sub>2</sub>CO<sub>3</sub> &amp; Na<sub>2</sub>SO<sub>4</sub></b>		
2		White liquor	As Na <sub>2</sub> O	
3		Na <sub>2</sub> S	171.875	lb
4		NaOH	515.625	lb
5		Na <sub>2</sub> CO <sub>3</sub>	57	lb
6		Na <sub>2</sub> SO <sub>4</sub>	9.44	lb
7				
8		<b>BASIS/ ASSUMPTION</b>		
9				
10		1 ton dry pulp	2000	lb
11		Yield	48	%
12		AA on od wood	16.5	%
13		WL activity	85	%
14		Sulfidity	25	%
15		WL total alkali	7.5	lb/ft <sup>3</sup>
16		Excess lime factor	2	%
17		Availability lime	85	%
18		Solid in unwashed slurry	40	%
19		Sp. Gr. WL	1.13	
20		Na <sub>2</sub> SO <sub>4</sub> /Na <sub>2</sub> S	0.2	lb/lb
21		Grit in system/total grit produced	0.9	
22		Water density	62.4	lb/cft
23		Sp. Gr. GL	1.16	
24				
25		<b>Mud washer</b>		
26		Recirculated solids from kiln	10	%
27		Washed mud solids content at underflow	=C18	%
28		Sp. Gr. at mud washer underflow	1.01	
29		Density of chemical at mud washer underflow	1.6	lb/cft
30		Density of TTA at mud washer underflow	1.1	
31		Wash water	1900	lb
32				
33		<b>Mud filter</b>		
34		Feed solid	25	%
35		Filtrate discharge	75	%
36		Filter shower/filter discharge	1	
37				
38		<b>Kiln and calciner</b>		
39		Fuel requirement	=353/2000	lb fuel /lb CaO
40		Ratio of fuel/air	=353/5615	lb/lb
41				
42		<b>Scrubber</b>		
43		Water in scrubber to mud washer	3320	lb
44		Dilution water	4500	lb
45				



46	<b>Slaker/Causticizer</b>		
47	Make up lime	26.11	lb
48	Water evaporated	40	lb
49	Grit solids in purge	60	%
50			
51	<b>G L C</b>		
52	Density of chemical at dregs filter	12.2	lb/cft
53	Underflow Solids	8	%
54	G L dregs	7.22	lb
55	Assume no Na <sub>2</sub> SO <sub>4</sub> lost		
56			
57	<b>Dregs Filter</b>		
58	Dregs solids content	50	%
59	Wash water/dregs ratio	2.5	lb
60			
61	<b>Recovery boiler</b>		
62	Black liquor elemental composition		
63	Na	22	%
64	C	36.84	%
65	H	3.5	%
66	S	3	%
67	O	34.39	%
68	inert	0.27	%
69			
70	Solid Concentration	70	%
71	Humidity (lb moisture/ lb dry air)	0.015	
72	Black Liquor Heating Value	6300	BTU/lb BLS
73	Salt cake rate (Salt cake/ BLS)	0.03	lb/lb
74			
75	Dry Air composition		
76	O <sub>2</sub>	0.232	lb O <sub>2</sub> /lb air
77	N <sub>2</sub>	=1-C76	
78	Excess air in to system	15	%
79			
80	<i>Energy balance</i>		
81	Temp. of liquor from concentrator	220	F
82	Temp. of combustion air enters	300	F
83	Temp. of flue gas discharge	350	F
84	Temp. of smelt	1500	F
85	Temp of reference	77	F
86	Radiation loss	0.28	%
87	Unaccountable loss	2	%
88			
89			
90	<b>Concentrator</b>		
91	Steam Economy	1.8	
92	Solid conc. In	50	%
93	Steam Pressure	=160+14.696	psi
94	Steam Temperature	370.4	F
95	Enthalpy	1197.12	btu/lb
96			
97	<b>Evaporators</b>		
98	Steam Economy	4.8	
99	Solid conc. In	17	%
100	Steam Pressure	=31.5+14.696	psi
101	Steam Temperature	276	F
102	Enthalpy	1172.739	btu/lb

## 2. Base-Recovery boiler

A	B	C	D	E	F	G	H
1	Compound	MW			Black liquor composition		
2	Na2S	=46+32			Compound	%weight	
3	Na2SO4	=46+32+64			Na	=Base-Calculation 1C68	
4	NaCl	=23+35.5			K	0	
5	Na2CO3	=23+23+12+48			S	=Base-Calculation 1C71	
6	K2CO3	=39+39+12+48			C	=Base-Calculation 1C69	
7	CO2	=12+32			H	=Base-Calculation 1C70	
8	H2O	=18			O	=Base-Calculation 1C72	
9					Cl	0	
10					inert	=Base-Calculation 1C73	
11					total	=SUM(G3:G10)	
12	Salt cake composition						
13	Na	=46/142*100	%				
14	S	=32/142*100	%				
15	O	=64/142*100	%				
16	total	=C15+C14+C13	%				
17							
18	MATERIAL BALANCE						
19	Assumption						
20	Reduction Eff.	=Base-Calculation 1C399	%				
21	Excess air	=Base-Calculation 1C382	%				
22	Solids	=Base-Calculation 1C75	%				
23	Humidity (lb H2O/lb dry air humidity)	=Base-Calculation 1C76					
24	Basis	1	lb of dry solid				
25	Salt cake rate	=Entry & Assumption 1C73					
26							
27							
28	Compound	Amount	O2 needed				
29	Na2S	=C24*C20/100*78/32*(G5/100+C25*C14/100)	0				
30	Na2SO4	=C24*142/32*(1-C20/100)*(G5/100+C25*C14/100)	=64/142*C30				
31							
32	Na2CO3	=C24*106/46*(G3/100-46/32*G5/100)	=C32*48/106				
33							
34	CO2	=44/12*(G6/100*C24-12/106*C32)	=32/44*C34				
35	H2O	=C24*18/2*G7/100	=16/18*C35				
36		Sum of O2	=SUM(D29:D35)				
37							
38	O2 inlet	=C41*0.232					
39	Water in liquor	=100-C22/C22*C24					
40	Theoretical air	=1036-G8/100*C24-C15/100*C25*C24/0.232					
41	Total air	=C40*(1+C21/100)					
42	N2 in flue gas	=C41*0.768					
43	O2 in flue gas	=1036-G8/100*C24-C15/100*C25*C24/C21/100					
44	Dry flue gas	=C43+C42+C34					
45	H2O in flue gas	=C35+(100-C22)/C22*C24+C41*C23					

35



	A	B	C	D	E	F
137		<b>ENERGY BALANCE</b>				
138		Temp. of liquor from concentrator	=Entry & Assumption!C81	F		
139		Temp. of combustion air enters	=Entry & Assumption!C82	F		
140		Temp. of flue gas discharge	=Entry & Assumption!C83	F		
141		Temp. of smelt	=Entry & Assumption!C84	F		
142		Temp of reference	=Entry & Assumption!C85	F		
143		Radiation loss	=Entry & Assumption!C86	%		
144		Unaccountable loss	=Entry & Assumption!C87	%		
145		Specific heat constant	=0.9886+4.444*10^-5*C138-(0.6276-3.557*10^-4*C138)*C92/100	Btu/lb F		
146						
147		<b>Heat input</b>	Amount	unit		%
148	1	Heating value of BLS	=Base-Calculation !C421	Btu/lb solids		=C148/\$C\$154*100
149						
150	2	Sensible heat in black liquor	=100/C22*C145*(C138-C142)	Btu/lb solids		=C150/\$C\$154*100
151						
152	3	Sensible heat in air	=SUM(D50:D52)*0.24*(C139-C142)	Btu/lb solids		=C152/\$C\$154*100
153						
154		Total heat input	=C152+C150+C148	Btu/lb solids		=C154/\$C\$154*100
155						
156		<b>Heat Output</b>				
157	1	Sensible heat in dry flue gas	=SUM(H50:H52)*0.24*(C140-C142)	Btu/lb solids		=C157/\$C\$175*100
158						
159	2	Sensible heat in moisture in flue gas	=H53*0.45*(C140-C142)	Btu/lb solids		=C159/\$C\$175*100
160						
161	3	Latent heat of water in black liquor	=(100-C22)/C22*1030	Btu/lb solids		=C161/\$C\$175*100
162						
163	4	Latent heat of water from combustion	=(H53-D52-D63)*1030	Btu/lb solids		=C163/\$C\$175*100
164						
165	5	Heat content of smelt	=H55*(580+0.4*(C141-1500))	Btu/lb solids		=C165/\$C\$175*100
166						
167	6	Heat to form sulfide	=H56*5550	Btu/lb solids		=C167/\$C\$175*100
168						
169	7	Radiation loss	=C154*C143/100	Btu/lb solids		=C169/\$C\$175*100
170						
171	8	Unaccountables	=C154*C144/100	Btu/lb solids		=C171/\$C\$175*100
172						
173	9	Heat to steam	=C154-SUM(C157,C159,C161,C163,C165,C167,C169,C171)	Btu/lb solids		=C173/\$C\$175*100
174						
175		Total Heat Output	=SUM(C157,C159,C161,C163,C165,C167,C169,C171,C173)	Btu/lb solids		=C175/\$C\$175*100
176						
177		Total Heat to steam energy	=C173*D86	BTU		

### 3. Base-Calculation

	A	B	C	D
1		Species	MW	
2		Na <sub>2</sub> O	=23+23+16	
3		NaOH	=23+16+1	
4		Na <sub>2</sub> S	=23+23+32	
5		Na <sub>2</sub> CO <sub>3</sub>	=23+23+12+48	
6		Na <sub>2</sub> SO <sub>4</sub>	=46+32+64	
7		Water	=16+2	
8		CaO	=40+16	
9		CaCO <sub>3</sub>	=40+12+48	
10		Ca(OH) <sub>2</sub>	=40+32+2	
11		CO <sub>2</sub>	44	
12				
13		<b>BASIS/ ASSUMPTION</b>		
14				
15		1 ton dry pulp	=Entry & Assumption!C10	lb
16		Yield	=Entry & Assumption!C11	%
17		AA on od wood	=Entry & Assumption!C12	%
18		WL activity	=Entry & Assumption!C13	%
19		Sulfidity	=Entry & Assumption!C14	%
20		WL total alkali	=Entry & Assumption!C15	
21		Excess lime factor	=Entry & Assumption!C16	%
22		Availability lime	=Entry & Assumption!C17	%
23		Solid in unwashed slurry	=Entry & Assumption!C18	%
24		Sp. Gr. WL	=Entry & Assumption!C19	
25		Na <sub>2</sub> SO <sub>4</sub> /Na <sub>2</sub> S	=Entry & Assumption!C20	
26		Grit in system/total grit produced	=Entry & Assumption!C21	
27		Water density	=Entry & Assumption!C22	lb/cft
28		Sp. Gr. GL	=Entry & Assumption!C23	
29				
30		<b>Mud washer</b>		
31		Recirculated solids from kiln	=Entry & Assumption!C26	%
32		Washed mud solids content at underflow	=C23	%
33		Sp. Gr. at mud washer underflow	=Entry & Assumption!C28	
34		Density of chemical at mud washer underflow	=Entry & Assumption!C29	lb/cft
35		Density of TTA at mud washer underflow	=Entry & Assumption!C30	
36		Wash water	=Entry & Assumption!C31	lb
37				
38		<b>Mud filter</b>		
39		Feed solid	=Entry & Assumption!C34	%
40		Filtrate discharge	=Entry & Assumption!C35	%
41		Filter shower/filter discharge	=Entry & Assumption!C36	
42				
43		<b>Kiln and calciner</b>		
44		Fuel requirement	=Entry & Assumption!C39	/lb CaO
45		Ratio of fuel/air	=Entry & Assumption!C40	

46			
47		<b>Scrubber</b>	
48		Water in scrubber to mud wash	=Entry & Assumption!C43
49		Dilution water	=Entry & Assumption!C44
50			
51		<b>Slaker/Causticizer</b>	
52		Make up lime	=Entry & Assumption!C47
53		Water evaporated	=Entry & Assumption!C48
54		Grits solids in purge	=Entry & Assumption!C49
55			
56		<b>G L C</b>	
57		Density of chemical at dreg filter	=Entry & Assumption!C52
58		Underflow Solids	=Entry & Assumption!C53
59		G L dreg	=Entry & Assumption!C54
60		Assume no Na2SO4 lost	=Entry & Assumption!C55
61			
62		<b>Dreg Filter</b>	
63		Dreg solids content	=Entry & Assumption!C58
64		Wash water/dreg ratio	=Entry & Assumption!C59
65			
66		<b>Recovery boiler</b>	
67		Black liquor elemental composition	
68		Na	=Entry & Assumption!C63
69		C	=Entry & Assumption!C64
70		H	=Entry & Assumption!C65
71		S	=Entry & Assumption!C66
72		O	=Entry & Assumption!C67
73		inert	=Entry & Assumption!C68
74			
75		Solid Concentration	=Entry & Assumption!C70
76		Humidity (lb moisture/ lb dry air)	=Entry & Assumption!C71
77			
78			
79		Dry Air composition	
80		O2	=Entry & Assumption!C76
81		N2	=Entry & Assumption!C77
82		Excess air in to system	=Entry & Assumption!C78
83			
84		<b>Concentrator</b>	
85		Steam Economy	=Entry & Assumption!C91
86		Solid conc.	=Entry & Assumption!C92
87			
88		<b>Evaporators</b>	
89		Steam Economy	=Entry & Assumption!C98
90		Solid conc.	=Entry & Assumption!C99

A	B	C	D	E	F
Stream no	Description	Amount	Unit	as Na2O	Unit
93	White liquor clarifier				
94	AA as Na2O	=C15/C16*100*C17/100			
95	TA	=C95/C18*100			
96	Volume of white liquor to digester	=C96/C20	cft		
97	Causticizing efficiency	=(E104-E314)/(E104+E105-E314)*100	%		
98	White liquor to digester	=C24*C97*C27	lb		
99	Degree of Conversion	=-0.0011082*(C20/0.06243)^2 + 0.087307*(C20/0.06243) + 95.243	%		
100	Total dissolved solids in white liquor	=C106+C105+C104+C103	lb		
101	White liquor to WL storage				
102	Na2S	=E103/C2*C4	lb	=C95*(C19/100)	lb
103	NaOH	=E104/C2*C3*2	lb	=C95-E103	lb
104	Na2CO3	=E105/C2*C5	lb	=C96-C95	lb
105	Na2SO4	=C103*C25	lb	=C106/C6*C2	lb
106					
107	Water	=C99-C101	lb		
108					
109	Available lime for causticizing	=C104/C3/2*C8*(1+C21/100)	lb		
110	Total lime require	=C110/C22*100	lb		
111	Total grit from unavaible lime	=C111-C110	lb		
112	Grit remaining in system	=C26*C112	lb		
113	Grit leaving system at classifier	=C112-C113	lb		
114	Excess Ca(OH)2 formed in slaker	=C21/100*C104/C3/2*C10	lb		
115	Total CaCO3 formed in causticizing	=C104/C3/2*C9	lb		
116	Water reacting to slake CaO	=C110/C8*C7	lb		
117	Total lime mud solids	=C116+C115+C113	lb		
118	Total unwashed mud slurry	=C118/C23*100	lb		
119	Total WL in unwashed mud slurry	=C119-C118	lb		
120					
121					
122	White liquor clarifier underflow (lime mud)				
123	Na2S	=E123/C2*C4	lb	=\$C\$120/\$C\$99*E103	lb
124	NaOH	=E124/C2*C3*2	lb	=\$C\$120/\$C\$99*E104	lb
125	Na2CO3	=E125/C2*C5	lb	=\$C\$120/\$C\$99*E105	lb
126	Na2SO4	=E126/C2*C6	lb	=\$C\$120/\$C\$99*E106	lb
127	CaCO3	=C116	lb		
128	Ca(OH)2	=C115	lb		
129	Inert	=C113	lb		
130	Water	=C120/C99*C108	lb		
131	total out	=SUM(C123:C130,C108,C103,C106)	lb	=SUM(E123:E126,E103:E106)	lb
132					
133	Unclarified white liquor				
134	Na2S	=C123+C103	lb	=C134/C4*C2	lb
135	NaOH	=C124+C104	lb	=C135/C3/2*C2	lb
136	Na2CO3	=C125+C105	lb	=C136/C5*C2	lb
137	Na2SO4	=C126+C106	lb	=C137/C6*C2	lb



453		<b>total out</b>	=SUM(C448:C452,C442:C445)	lb		
454						
455						
456		Energy usage	=C469*Entry & Assumption1C95	BTU		
457		<b>Concentrators</b>				
458						
459	4	Black liquor solid to concentrators				
460		Na	=C475	lb		
461		C	=C476	lb		
462		H	=C477	lb		
463		S	=C478	lb		
464		O	=C479	lb		
465		Inert	=C480	lb		
466		H2O	=C473/C86*100-C473	lb		
467						
468	5	Steam requirement for concentrator				
469		Steam	=C466/C85	lb		
470						
471		<b>total in</b>	=SUM(C460:C466,C469)	lb		
472						
473		total black liquor solids	=SUM(C475:C480)			
474	7	Black liquor to recovery boiler				
475		Na	=C424	lb		
476		C	=C425	lb		
477		H	=C426	lb		
478		S	=C427	lb		
479		O	=C428	lb		
480		Inert	=C429	lb		
481		H2O	=C430	lb		
482						
483	6	Condensate from Concentrators				
484		Water	=C466-C481	lb		
485		Steam	=C469	lb		
486						
487		<b>total out</b>	=SUM(C484:C485,C475:C481)	lb		
488						
489						
490		Energy usage	=C503*Entry & Assumption1C102	BTU		
491		<b>Evaporators</b>				
492						
493	1	Black liquor solid from washer				
494		Na	=C460	lb		
495		C	=C461	lb		
496		H	=C462	lb		
497		S	=C463	lb		

138	CaCO3	=C127	lb		
139	Ca(OH)2	=C128	lb		
140	Inert	=C129	lb		
141	Water	=C130+C108	lb		
142	<b>total in</b>	<b>=SUM(C134:C141)</b>	<b>lb</b>	<b>=SUM(E134:E137)</b>	<b>lb</b>
143					
144					
145	<b>Mud washer</b>				
146					
147	15 Fresh water dilution				
148	Water	=C36	lb		
149					
150	23 Recirculated from mud filter				
151	NaOH	=C179	lb	=E179	lb
152	Na2S	=C180	lb	=E180	lb
153	Na2CO3	=C181	lb	=E181	lb
154	Na2SO4	=C182	lb	=E182	lb
155	Water	=C209	lb		
156					
157	29 Recycle from recycle tank				
158	CaCO3	=C31/100*C168	lb		
159	Ca(OH)2	=C31/100*C169	lb		
160	Inert	=C31/100*C170	lb		
161	Water	=C48	lb		
162					
163	18 White liquor clarifier underflow (lime mud)				
164	Na2S	=C123	lb	=E123	lb
165	NaOH	=C124	lb	=E124	lb
166	Na2CO3	=C125	lb	=E125	lb
167	Na2SO4	=C126	lb	=E126	lb
168	CaCO3	=C127	lb		
169	Ca(OH)2	=C128	lb		
170	Inert	=C129	lb		
171	Water	=C130	lb		
172	<b>total in</b>	<b>=SUM(C164:C171,C158,C161,C151,C155,C148)</b>	<b>lb</b>	<b>=SUM(E164:E167,E151:E154)</b>	<b>lb</b>
173					
174	Total underflow	=(C183+C184+C185)/C32*100	lb		
175	Liquor	=C174-(C183+C184+C185)	lb		
176	Weight of chemical	=C175/C27*C34/C33	lb		
177	TTA			=C175/C33/C27*C35	lb
178	16 Underflow from mud washer				
179	Na2S	=E179/C2*C4	lb	=\$E\$177*0.7185	lb
180	NaOH	=E180/C2*C3*2	lb	=\$E\$177*0.21875	lb
181	Na2CO3	=E181/C2*C5	lb	=\$E\$177*0.0625	lb
182	Na2SO4	=E182/C2*C6	lb	0	lb

183		CaCO3	= (100+\$C\$31)/100*(C168)	lb		
184		Ca(OH)2	= (100+\$C\$31)/100*(C169)	lb		
185		Inert	= (100+\$C\$31)/100*(C170)	lb		
186		Water	=C175-C176	lb		
187						
188	14	Overflow to weak wash storage				
189		Na2S	=C164+C151-C179	lb	=C189/\$C\$4*\$C\$2	lb
190		NaOH	=C165+C152-C180	lb	=C190/\$C\$3/2*\$C\$2	lb
191		Na2CO3	=C166+C153-C181	lb	=C191/\$C\$5*\$C\$2	lb
192		Na2SO4	=C167+C154-C182	lb	=C192/\$C\$6*\$C\$2	lb
193		Water	=C171+C161+C155+C148-C186	lb		
194		<b>total out</b>	=SUM(C189:C193,C179:C186)	lb	=SUM(E189:E192,E179:E182)	lb
195						
196						
197		<b>Mud filter</b>				
198						
199		Mud solids	= (100+C31)/100*C118	lb		
200		Total feed flow	=C199/C39*100			
201	20	Feed to mud filter				
202		Na2S	=C179	lb	=C202/\$C\$4*\$C\$2	lb
203		NaOH	=C180	lb	=C203/\$C\$3/2*\$C\$2	lb
204		Na2CO3	=C181	lb	=C204/\$C\$5*\$C\$2	lb
205		Na2SO4	=C182	lb	=C205/\$C\$6*\$C\$2	lb
206		CaCO3	=C183	lb		
207		Ca(OH)2	=C184	lb		
208		Inert	=C185	lb		
209		Water	=C200-C199	lb		
210						
211	21	Filter showers				
212		Water	=C219*C41	lb		
213		<b>total in</b>	=SUM(C212,C202:C209)	lb	=SUM(E202:E205)	lb
214						
215		Total feed to kiln	=C199/C40*100	lb		
216	22	Feed to kiln				
217		CaCO3	=C206+C207	lb		
218		Inert	=C208	lb		
219		Water	=C215-C199	lb		
220						
221	23	Recirculated from mud filter				
222		Na2S	=C202	lb	=C222/\$C\$4*\$C\$2	lb
223		NaOH	=C203	lb	=C223/\$C\$3/2*\$C\$2	lb
224		Na2CO3	=C204	lb	=C224/\$C\$5*\$C\$2	lb
225		Na2SO4	=C205	lb	=C225/\$C\$6*\$C\$2	lb
226		Water	=C212+C209-C219	lb		
227		<b>total out</b>	=SUM(C222:C226,C217:C219)	lb	=SUM(E222:E225)	lb

228					
229					
230		<b>Kiln and calciner</b>			
231		CaCO <sub>3</sub> → CaO+CO <sub>2</sub>			
232					
233	22	Feed to kiln			
234		CaCO <sub>3</sub>	=C217	lb	
235		Inert	=C218	lb	
236		Water	=C219	lb	
237					
238	24	Fuel + air			
239		Fuel	=C44*C244	lb	
240		Air	=C239/C45	lb	
241		<b>total in</b>	=SUM(C234:C236,C239:C240)	lb	
242					
243	25	Reburned lime feed			
244		CaO	=C110-C52	lb	
245		Inert	=C112	lb	
246					
247	26	Underflow to scrubber			
248		Dust	=C234-C244/56*100-C245+C235	lb	
249		CO <sub>2</sub>	=C244/56*44	lb	
250		Combustion product	=C239+C240	lb	
251		Water	=C236	lb	
252		<b>total out</b>	=SUM(C248:C251,C244:C245)	lb	
253					
254					
255		<b>Scrubber Stacks</b>			
256					
257	26	Underflow to scrubber			
258		Dust	=C248	lb	
259		CO <sub>2</sub>	=C249	lb	
260		Combustion product	=C250	lb	
261		Water	=C251	lb	
262					
263	28	Dilution water			
264		Water	=C49	lb	
265		<b>total in</b>	=SUM(C258:C261,C264)	lb	
266					
267	27	Vent gas			
268		Dust	=C258-C274	lb	
269		CO <sub>2</sub>	=C259	lb	
270		Combustion product	=C260	lb	
271		Water	=C264-C275+C261	lb	
272					

273	29	Recycle from recycle tank				
274		Solids	=C158+C159+C160	lb		
275		Water	=C48	lb		
276		<b>total out</b>	<b>=SUM(C268:C271,C274,C275)</b>	<b>lb</b>		
277						
278						
279		<b>Slaker/ Causticizer</b>				
280		CaO + H2O --> Ca(OH)2				
281		Ca(OH)2 + Na2CO3 --> 2NaOH + CaCO3				
282		NaCO3 reacted	=C291/100*106	lb		
283		NaOH formed	=C291/100*40*2	lb		
284		Water reacted	=C291/100*18+C292/74*18	lb		
285		Available lime for causticizing	=C306+C310	lb		
286	39	Unclarified white liquor				
287		Na2S	=C134	lb	=C287/SC\$4*SC\$2	lb
288		NaOH	=C135	lb	=C288/SC\$3/2*SC\$2	lb
289		Na2CO3	=C136	lb	=C289/SC\$5*SC\$2	lb
290		Na2SO4	=C137	lb	=C290/SC\$6*SC\$2	lb
291		CaCO3	=C138	lb		
292		Ca(OH)2	=C139	lb		
293		Inert	=C140	lb		
294		Water	=C141	lb		
295						
296		Total purge grits	=C298/C54*100	lb		
297	36	Grit to discharge				
298		Inerts	=C114	lb		
299		Water	=C296-C298	lb		
300						
301	37	Water evaporated				
302		Water	=C53	lb		
303		<b>total out</b>	<b>=SUM(C302,C298:C299,C287:C294)</b>	<b>lb</b>	<b>=SUM(E287:E290)</b>	<b>lb</b>
304						
305	25	Reburned lime feed				
306		CaO	=C244	lb		
307		Inert	=C245	lb		
308						
309	35	Make up lime				
310		CaO	=C52	lb		
311						
312	34	Clarified green liquor feed				
313		Na2S	=C287	lb	=C313/SC\$4*SC\$2	lb
314		NaOH	=C288-C283	lb	=C314/SC\$3/2*SC\$2	lb
315		Na2CO3	=C289+C282	lb	=C315/SC\$5*SC\$2	lb
316		Na2SO4	=C290	lb	=C316/SC\$6*SC\$2	lb
317		Water	=C302+C299+C294+C284	lb		

318		<b>total in</b>	=SUM(C306:C307,C310,C313,C317)	lb	=SUM(E313,E316)	lb
319						
320						
321		<b>Green Liquor Clarifier</b>				
322						
323	13	Unclarified green liquor from smelt tank				
324		Dreg	=C59	lb		
325		Na2S	=C344+C356-C332	lb	=C325/SC\$4*SC\$2	lb
326		NaOH	=C345+C357-C333	lb	=C326/SC\$3/2*SC\$2	lb
327		Na2CO3	=C346+C358-C334	lb	=C327/SC\$5*SC\$2	lb
328		Na2SO4	=C347+C359-C335	lb	=C328/SC\$6*SC\$2	lb
329		Water	=C349+C360-C336	lb		
330						
331	30	Filtrate to GLC				
332		Na2S	=C344	lb	=E344	lb
333		NaOH	=C345	lb	=E345	lb
334		Na2CO3	=C346	lb	=E346	lb
335		Na2SO4	=C347	lb	=E347	lb
336		Water	=C387	lb		
337		<b>total in</b>	=SUM(C332:C336,C324:C329)	lb	=SUM(E325,E328,E332,E335)	lb
338						
339		Total underflow to dreg filter	=C59/C58*100	lb		
340		Liquor in underflow	=C339-C59	lb		
341		Weight of chemical in underflow	=C340/C27/C28*C57	lb		
342		TTA			=C340/C27/C28*C18	lb
343	32	Underflow to dreg filter				
344		Na2S	=E344/C2*C4	lb	=0.1*\$E\$342	lb
345		NaOH	=E345/C2*C3*2	lb	=0.2*\$E\$342	lb
346		Na2CO3	=E346/C2*C5	lb	=0.7*\$E\$342	lb
347		Na2SO4	=E347	lb	0	lb
348		Dreg	=C324	lb		
349		Water	=C340-C341	lb		
350						
351		GL TTA	=E356+E357+E358	lb		
352		Volume GL	=C351/C20	cft		
353		Sulphidity	=E356/C351*100	%		
354		AA in GL	=(E356+E357)/C352	lb/cft		
355	34	Clarified green liquor feed				
356		Na2S	=C313	lb	=C356/SC\$4*SC\$2	lb
357		NaOH	=C314	lb	=C357/SC\$3/2*SC\$2	lb
358		Na2CO3	=C315	lb	=C358/SC\$5*SC\$2	lb
359		Na2SO4	=C316	lb	=C359/SC\$6*SC\$2	lb
360		Water	=C317	lb		
361		<b>total out</b>	=SUM(C356:C360,C344:C349)	lb	=SUM(E356,E359,E344,E347)	lb
362						

363					
364		<b>Dregs filter</b>			
365					
366	31	Wash water			
367		Water	=C64*C374	lb	
368					
369	32	Underflow to dreg filter			
370		Na2S	=C344	lb	=E344
371		NaOH	=C345	lb	=E345
372		Na2CO3	=C346	lb	=E346
373		Na2SO4	=C347	lb	=E347
374		Dreg	=C348	lb	
375		Water	=C349	lb	
376		<b>total in</b>	=SUM(C370:C375,C367)	lb	=SUM(E370:E373)
377					
378	33	Dregs to discharge			
379		Dreg	=C374	lb	
380		Water	=C379/C63*100-C379	lb	
381					
382	30	Filtrate to GLC			
383		Na2S	=C370	lb	=E370
384		NaOH	=C371	lb	=E371
385		Na2CO3	=C372	lb	=E372
386		Na2SO4	=C373	lb	=E373
387		Water	=C367+C375-C380	lb	
388		<b>total out</b>	=SUM(C379:C380,C383:C387)	lb	=SUM(E382:E385)
389					
390					
391		<b>Smelt tank</b>			
392	14	Overflow to weak wash storage			
393		Na2S	=C189	lb	=E189
394		NaOH	=C190	lb	=E190
395		Na2CO3	=C191	lb	=E191
396		Na2SO4	=C192	lb	=E192
397		Water	=C193	lb	
398					
399		% Reduction	=E402/(E402+E405)*100	%	
400	11	Smelt from furnace			
401		Dreg	=C413	lb	
402		Na2S	=C414-C393	lb	=C402/SC\$4*SC\$2
403		NaOH	=C415-C394	lb	=C403/SC\$3/2*SC\$2
404		Na2CO3	=C416-C395	lb	=C404/SC\$5*SC\$2
405		Na2SO4	=C417-C396	lb	=C405/SC\$6*SC\$2
406					
407		<b>total in</b>	=SUM(C401:C405,C393:C397)	lb	=SUM(E402:E405,E393:E396)

408					
409	12	Scrubber stack loss			
410		Water	=C397-C418	lb	
411					
412	13	Unclassified green liquor from smelt tank			
413		Dreg	=C324	=D324	
414		Na2S	=C325	=D325	=F325
415		NaOH	=C326	=D326	=F326
416		Na2CO3	=C327	=D327	=F327
417		Na2SO4	=C328	=D328	=F328
418		Water	=C329	=D329	
419		<b>total out</b>	<b>=SUM(C413:C418,C410)</b>	<b>lb</b>	<b>=SUM(E414:E417)</b>
420					
421		Black Liquor Heating Value	=Entry & Assumption!C72	BTU/lb	
422		<b>Recovery boiler</b>			
423	7	Black liquor to recovery boiler			
424		Na	=Base-Recovery Boiler!D127	lb	
425		C	=Base-Recovery Boiler!D129	lb	
426		H	=Base-Recovery Boiler!D130	lb	
427		S	=Base-Recovery Boiler!D128	lb	
428		O	=Base-Recovery Boiler!D131	lb	
429		Inert	=Base-Recovery Boiler!D132	lb	
430		H2O	=Base-Recovery Boiler!D133	lb	
431					
432	8	Salt cake			
433		Na2SO4	=Base-Recovery Boiler!D125	lb	
434					
435	9	Air			
436		N2	=Base-Recovery Boiler!D120	lb	
437		O2	=Base-Recovery Boiler!D121	lb	
438		H2O	=Base-Recovery Boiler!D122	lb	
439		<b>total in</b>	<b>=SUM(C436:C438,C433,C424,C430)</b>	<b>lb</b>	
440					
441	10	Flue gas			
442		N2	=Base-Recovery Boiler!H121	lb	
443		O2	=Base-Recovery Boiler!H122	lb	
444		CO2	=Base-Recovery Boiler!H120	lb	
445		H2O	=Base-Recovery Boiler!H123	lb	
446					
447	11	Smelt from furnace			
448		Na2S	=Base-Recovery Boiler!H126	lb	
449		NaOH	=C403	lb	
450		Na2CO3	=Base-Recovery Boiler!H129	lb	
451		Na2SO4	=Base-Recovery Boiler!H127	lb	
452		Inert	=Base-Recovery Boiler!H130	lb	



453		<b>total out</b>	=SUM(C448:C452,C442:C445)	lb
454				
455				
456		Energy usage	=C469*Entry & Assumption!C95	BTU
457		<b>Concentrators</b>		
458				
459	4	Black liquor solid to concentrators		
460		Na	=C475	lb
461		C	=C476	lb
462		H	=C477	lb
463		S	=C478	lb
464		O	=C479	lb
465		Inert	=C480	lb
466		H2O	=C473/C86*100-C473	lb
467				
468	5	Steam requirement for concentrator		
469		Steam	=C466/C85	lb
470				
471		<b>total in</b>	=SUM(C460:C466,C469)	lb
472				
473		total black liquor solids	=SUM(C475:C480)	
474	7	Black liquor to recovery boiler		
475		Na	=C424	lb
476		C	=C425	lb
477		H	=C426	lb
478		S	=C427	lb
479		O	=C428	lb
480		Inert	=C429	lb
481		H2O	=C430	lb
482				
483	6	Condensate from Concentrators		
484		Water	=C466-C481	lb
485		Steam	=C469	lb
486				
487		<b>total out</b>	=SUM(C484:C485,C475:C481)	lb
488				
489				
490		Energy usage	=C503*Entry & Assumption!C102	BTU
491		<b>Evaporators</b>		
492				
493	1	Black liquor solid from washer		
494		Na	=C460	lb
495		C	=C461	lb
496		H	=C462	lb
497		S	=C463	lb
498		O	=C464	lb

499		Inert	=C465	lb
500		H2O	=C507/C90*100-C507	lb
501				
502	2	Steam requirement for evaporators		
503		Steam	=C500/C89	lb
504				
505		<b>total in</b>	<b>=SUM(C494:C500,C503)</b>	<b>lb</b>
506				
507		Total black liquor solids	=SUM(C509:C514)	
508	4	Black liquor solid to concentrators		
509		Na	=C494	lb
510		C	=C495	lb
511		H	=C496	lb
512		S	=C497	lb
513		O	=C498	lb
514		Inert	=C499	lb
515		H2O	=C466	lb
516				
517	3	Condensate from evaporators		
518		Water	=C500-C515	lb
519		Steam	=C503	lb
520				
521		<b>total out</b>	<b>=SUM(C518:C519,C509:C515)</b>	<b>lb</b>
522				

#### 4. Base-Overall Balance

IN			OUT		
Stream no	Description	Amount (lb)	Stream no	Description	Amount (lb)
1	=Base-Calculation 'B493		3	=Base-Calculation 'B517	
6	=Base-Calculation 'B494	=Base-Calculation 'C494		=Base-Calculation 'B518	=Base-Calculation 'C518
7	=Base-Calculation 'B495	=Base-Calculation 'C495		=Base-Calculation 'B519	=Base-Calculation 'C519
8	=Base-Calculation 'B496	=Base-Calculation 'C496			
9	=Base-Calculation 'B497	=Base-Calculation 'C497	6	=Base-Calculation 'B483	
10	=Base-Calculation 'B498	=Base-Calculation 'C498		=Base-Calculation 'B484	=Base-Calculation 'C484
11	=Base-Calculation 'B499	=Base-Calculation 'C499		=Base-Calculation 'B485	=Base-Calculation 'C485
12	=Base-Calculation 'B500	=Base-Calculation 'C500			
13			10	=Base-Calculation 'B441	
14	2 =Base-Calculation 'B502			=Base-Calculation 'B442	=Base-Calculation 'C442
15	=Base-Calculation 'B503	=Base-Calculation 'C503		=Base-Calculation 'B443	=Base-Calculation 'C443
16				=Base-Calculation 'B444	=Base-Calculation 'C444
17	5 =Base-Calculation 'B468			=Base-Calculation 'B445	=Base-Calculation 'C445
18	=Base-Calculation 'B469	=Base-Calculation 'C469			
19			12	=Base-Calculation 'B409	
20	8 =Base-Calculation 'B432			=Base-Calculation 'B410	=Base-Calculation 'C410
21	=Base-Calculation 'B433	=Base-Calculation 'C433			
22			27	=Base-Calculation 'B267	
23	9 =Base-Calculation 'B435			=Base-Calculation 'B268	=Base-Calculation 'C268
24	=Base-Calculation 'B436	=Base-Calculation 'C436		=Base-Calculation 'B269	=Base-Calculation 'C269
25	=Base-Calculation 'B437	=Base-Calculation 'C437		=Base-Calculation 'B270	=Base-Calculation 'C270
26	=Base-Calculation 'B438	=Base-Calculation 'C438		=Base-Calculation 'B271	=Base-Calculation 'C271
27					
28			33	=Base-Calculation 'B378	
29	15 =Base-Calculation 'B147			=Base-Calculation 'B379	=Base-Calculation 'C379
30	=Base-Calculation 'B148	=Base-Calculation 'C148		=Base-Calculation 'B380	=Base-Calculation 'C380
31					
32	19 fresh water addition before mud filter		36	=Base-Calculation 'B297	
33	Water	=Base-Calculation 'C209-E		=Base-Calculation 'B298	=Base-Calculation 'C298
34				=Base-Calculation 'B299	=Base-Calculation 'C299
35	21 =Base-Calculation 'B211				
36	=Base-Calculation 'B212	=Base-Calculation 'C212	37	=Base-Calculation 'B301	
37				=Base-Calculation 'B302	=Base-Calculation 'C302
38	24 =Base-Calculation 'B238				
39	=Base-Calculation 'B239	=Base-Calculation 'C239	40	=Base-Calculation 'B102	
40	=Base-Calculation 'B240	=Base-Calculation 'C240		=Base-Calculation 'B103	=Base-Calculation 'C103
41				=Base-Calculation 'B104	=Base-Calculation 'C104
42	28 =Base-Calculation 'B263			=Base-Calculation 'B105	=Base-Calculation 'C105
43	=Base-Calculation 'B264	=Base-Calculation 'C264		=Base-Calculation 'B106	=Base-Calculation 'C106
44				Water	=Base-Calculation 'C108
45	31 =Base-Calculation 'B366				
46	=Base-Calculation 'B367	=Base-Calculation 'C367			
47					
48	35 =Base-Calculation 'B309				
49	=Base-Calculation 'B310	=Base-Calculation 'C310			
50					
51	Total in	=SUM(C6:C49)		Total out	=SUM(H6:H44)

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